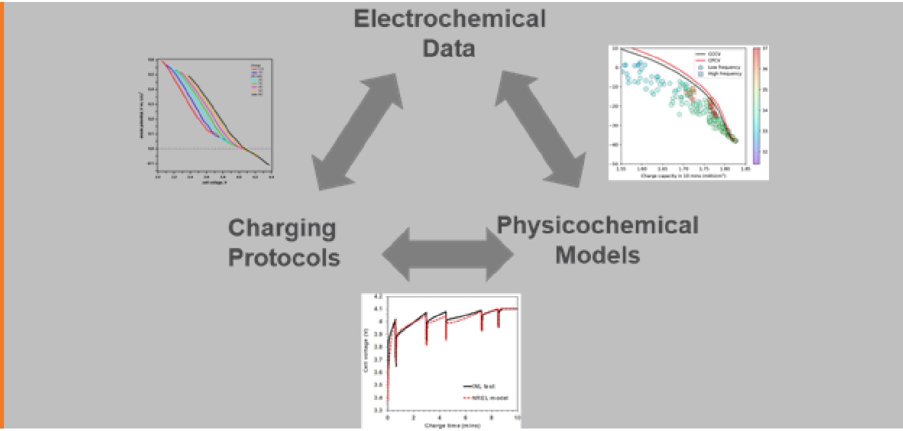
BAT462: AGING AND THE ROLE OF FAST-CHARGE PROTOCOLS



XCEL
eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

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Web Conference

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U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
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OVERVIEW

Timeline

- Start: October 1, 2017
- End: September 30, 2021
- Percent Complete: 75%

Barriers

- Cell degradation during fast charge
- Low energy density and high cost of fast charge cells

Budget

- Funding for FY20 – $5.6M

Partners

- Argonne National Laboratory
- Idaho National Laboratory
- Lawrence Berkeley National Lab
- National Renewable Energy Laboratory
- SLAC National Accelerator Lab
- Oak Ridge National Lab

RELEVANCE

Impact:

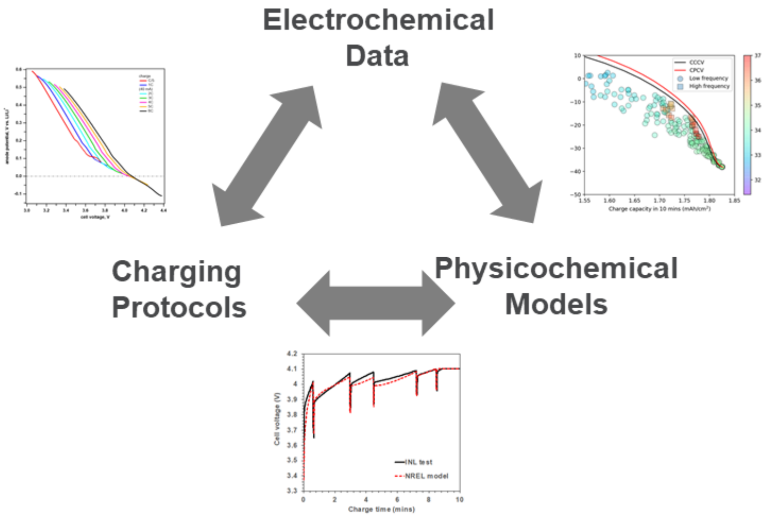
Understanding the impact of new charge protocols impacted by lack of clear methods and incomplete information

Enhanced knowledge can be gained by aligning key electrochemical data and physicochemical models to understand role of new protocols

Developed framework can be readily transitioned to other chemistries and cell designs

Objective

Aligning Models and Electrochemical Data to Enhance Understanding and Advance New Charge Protocols



TASK MILESTONES

Milestone	Lead	Due	Status
Metrics for comparing protocols	Dufek (INL)	12/31/19	Complete
Use existing models to down select protocols	Mai (NREL)	3/31/20	Complete
Create experimental matrix and initiate characterization	Dufek (INL), Bloom (Argonne)	6/30/20	In process
Refine model based on experimental data	Colclasure (NREL)	9/30/20	In process
Use best case protocols in conjunction with improved anode and electrolyte to test CAMP pouch cells	Dufek (INL), Bloom (Argonne)	9/30/20	Planned

APPROACH

Understand the role of different charge protocols

- Develop methods for comparison
- Refine physicochemical models to evaluate new protocols
- Transition protocols from model to electrochemical validation

Identify key barriers as different charge conditions are used

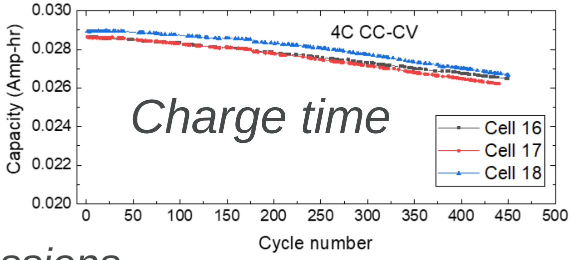
- Develop coin and three-electrode cell methods

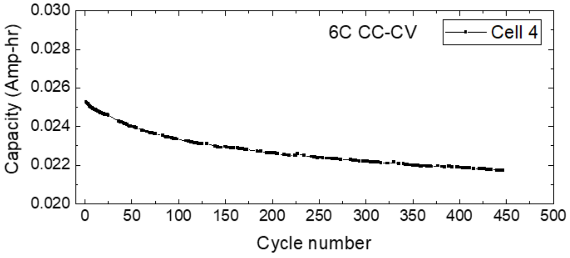
Transition lessons for full cell evaluation of updated cells near the end of FY-2020

COMPARING CHARGE PROTOCOLS

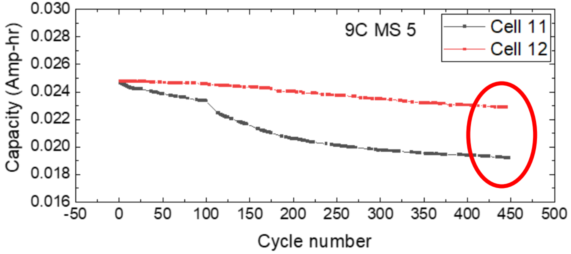
Round 2 Cells from CAMP

- Several protocols generate some positive results if just looking at capacity fade
- Need methods to more directly compare and contrast protocols
- Methods and metrics should expand scientific understanding of limitations

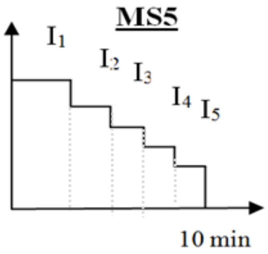




Active discussions on protocols with Behind-the-Meter Storage (Bat422) and DirectXFC (Elt257)



Variability



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PERFORMANCE METRICS FOR PROTOCOL IDENTIFICATION

Round 2 cells nominally ~200 Wh/kg depending on cell size and electrolyte content

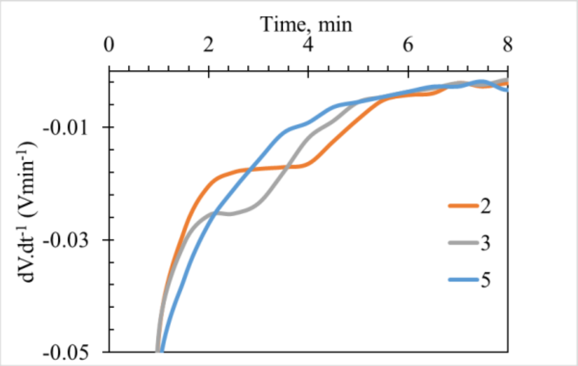
		6.8CCCV	6.8C MS2	9C CCCV	9CMS2	6C CCCV (rd2)	9C MS5 (rd2)	Ideal
BOL	% recharge in 10 min (based on C/2 discharge)	1.54	1.53	1.58	1.53	1.95	1.9	>1.9
BOL	Charge % during CV	16.8	7.4	31.7	5.1	38	5	<10
Cycle	Delta T (C) – Full cell & Model (starting from 25C)	NA	NA	NA	NA	NA	NA	
Cycle	Percent fade over 125 cycles	5	4	7	5	16	10	<7
Cycle	Variability at cycle 125	1	0	4	2	17	5	<2

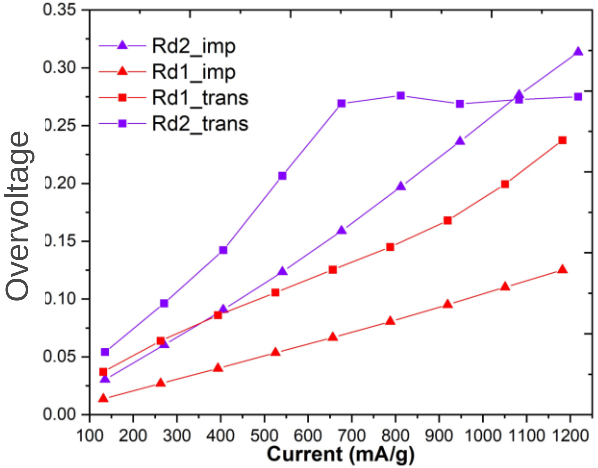
ADDITIONAL METRICS

dV/dt and Impedance Analysis

- Good indicator of mixed potential at the negative electrode
- As extent of Li plating increases becomes less distinct
- Need to directly follow on a cycle-by-cycle basis

Signal varies with cycling and more extensive Li plating





Comparisons need to be aligned based on normalized currents not necessarily C-rates

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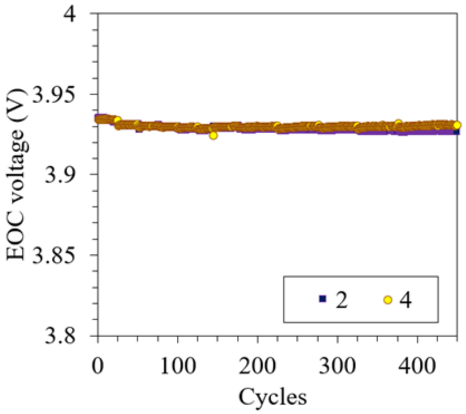
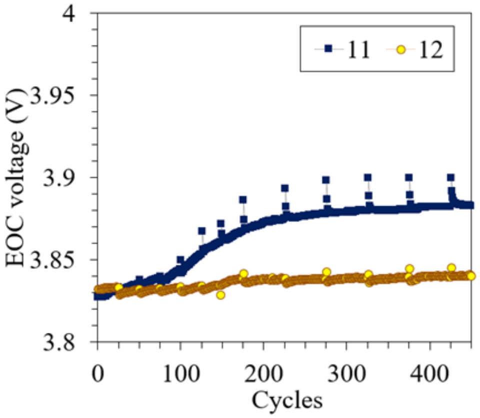
ADDITIONAL METRICS

End-of-charge Voltage

- Gradual decline indicative of normal aging (cathode loss, LLI etc.)
- Increase suggests mixed potential and increased Li plating
- Strong compliment of dV/dT and not limited to early cycling





Tanim et. al, *in preparation*

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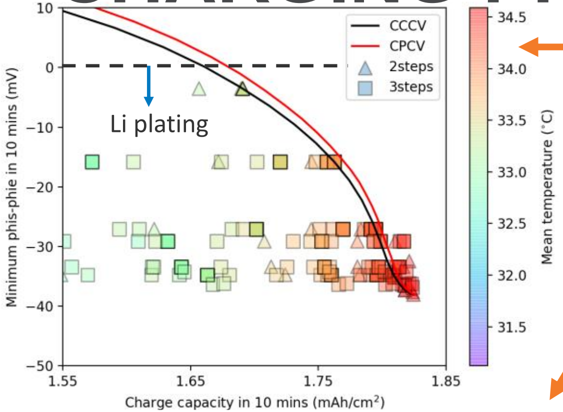
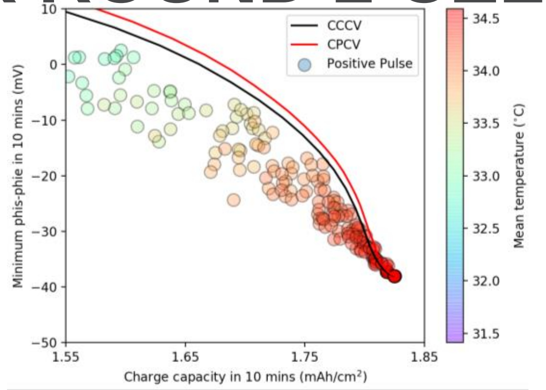
MODEL INVESTIGATION OF PROPOSED FAST CHARGING PROTOCOLS FOR ROUND 2 CELLS

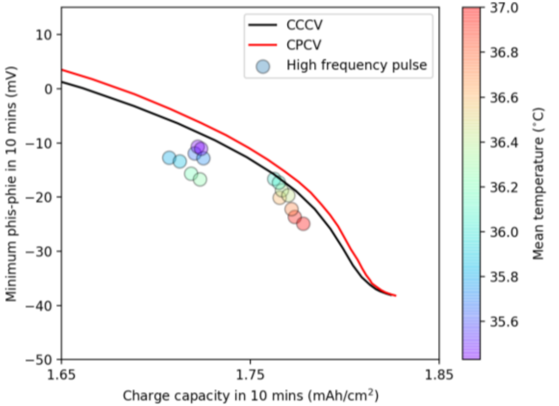


Multi-step investigated with constant 4.1V cutoff for all steps

Low Frequency Pulse: 20 to 100 s pulse

High Frequency Pulse: 0.5 to 2 s pulse





- Electrochemical modeling provides an effective screening tool for investigating large protocol space to limit required costly experiments
- Electrochemical model has been developed and validated with extensive testing with rates from C/20 to 9C and in custom 3-electrode setup/pouch cells
- Goal: Maximize capacity while avoiding lithium plating
- Often proposed protocols are ineffective because changes in current not informed by potential for lithium plating
- Note, optimizing pulse charging requires accurate lithium stripping model
- Optimizing multi-step protocol requires variable cutoff potential

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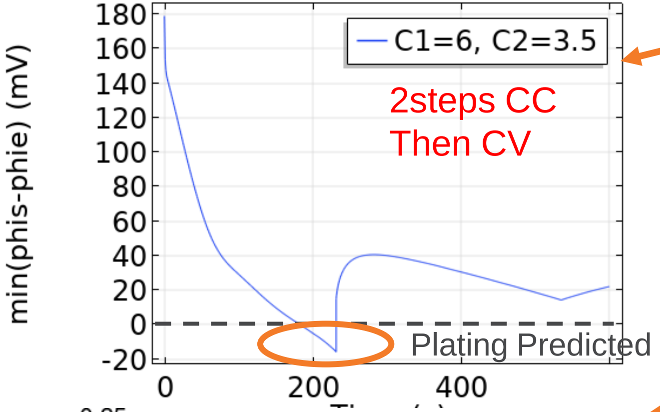
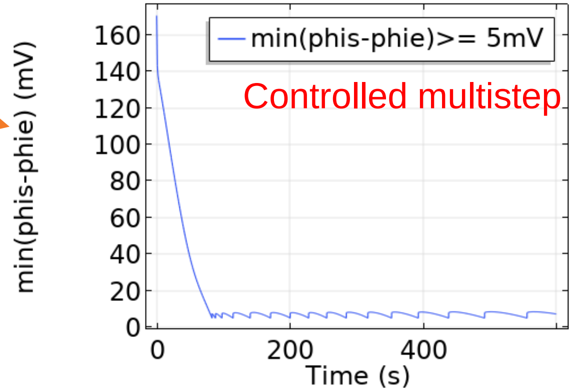
MODEL INFORMED DESIGN OF CHARGING PROTOCOL TO PREVENT LITHIUM PLATING

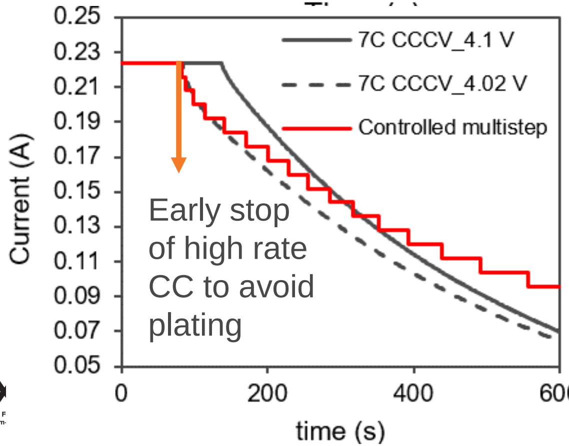


Plating potential during a 2-step protocol

Plating potential with current reduction from internal sensor

Current for internal sensor and 7CCCV





- Li plates when the cell is charged to high voltage at a high rate
- Assume an internal sensor monitors min(phis-phie) or potential for lithium plating
- Automatically steps down the charge current by 0.25C when min(phis-phie) is smaller than a critical value (5 mV)
- Charge to 4.1V at high rate causes plating
- Cell can handle higher current during CV

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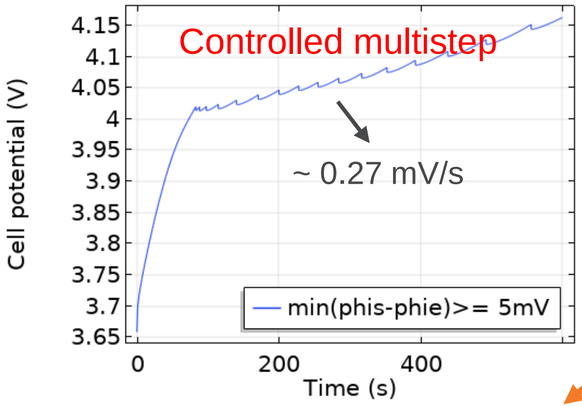
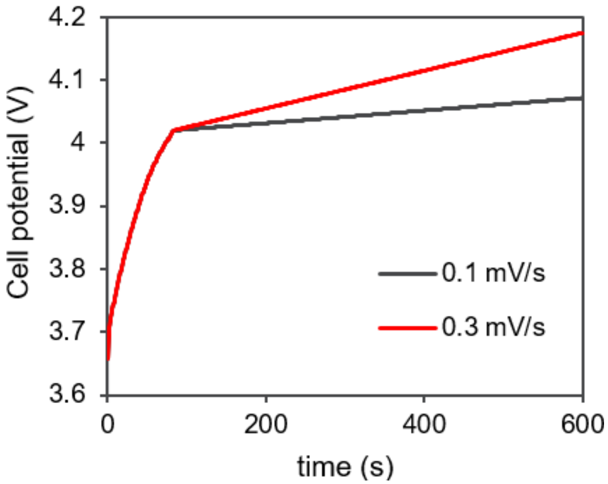
NOVEL PROTOCOL 1: CC + VOLTAGE RAMPING FOR ROUND 2 CELLS

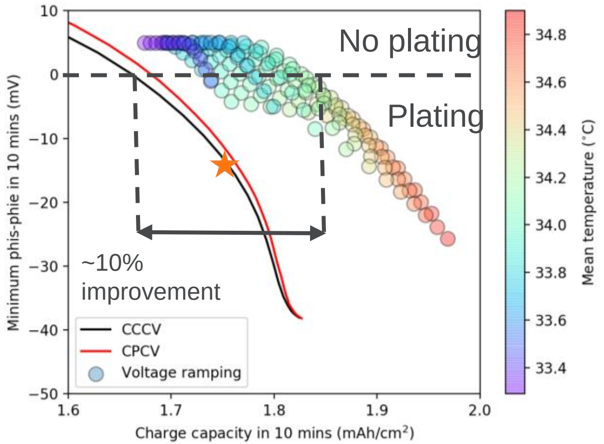


Voltage profile with "plating" sensor

Example voltage profile for ramp protocol



Ramp protocol parameter sweep compared to CCCV/CPCV



- The controlled multistep protocol gives improved performance but difficult to implement
- Voltage is fairly linear after the initial CC charge
- Performed large parameter sweeping:
  - First CC in (5C to10C, step=0.5C)
  - Transit to voltage ramping once min(phis-phie) <= 5mV
  - Voltage ramping rate in (0.1,0.4,step=0.025) mV/s
- Significant reduction of plating driving force

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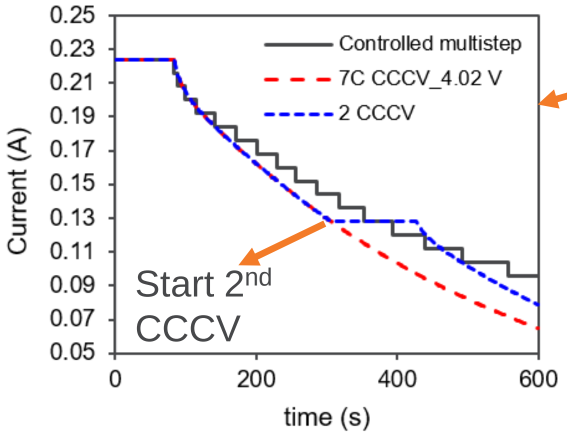
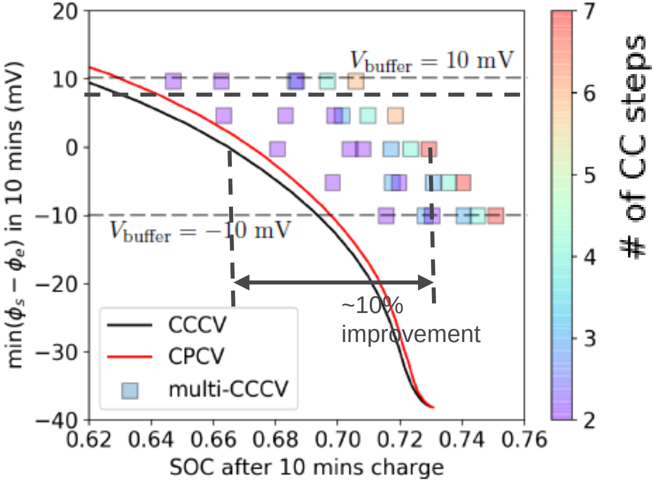
NOVEL PROTOCOL 2: MULTISTAGE CCCV FOR ROUND 2



Current for protocol with 2 CCCV steps compared to internal sensor

Parameter sweep for multi CCCV protocol



- Using multiple CC-CV steps with varying current and voltage cutoff can significantly improve charge capacity
- Significant reduction of lithium plating
- Initial 7C charging results shown (3 parameter sweep)
- 10.5% improvement in predicted capacity with 7 individual CC-CV steps
- 6.6% improvement in predicted capacity with 2 individual CC-CV steps
- Some current is removed from initial charging and more is applied in later stages

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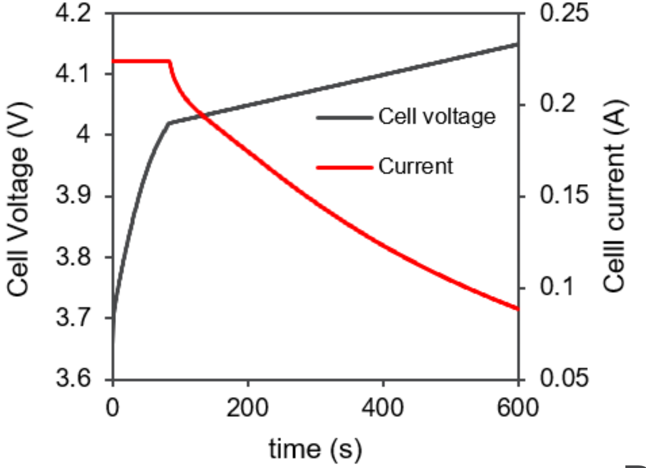
RAMP AND MULTI-CCCV SIGNIFICANTLY IMPROVE PLATING FREE CAPACITY

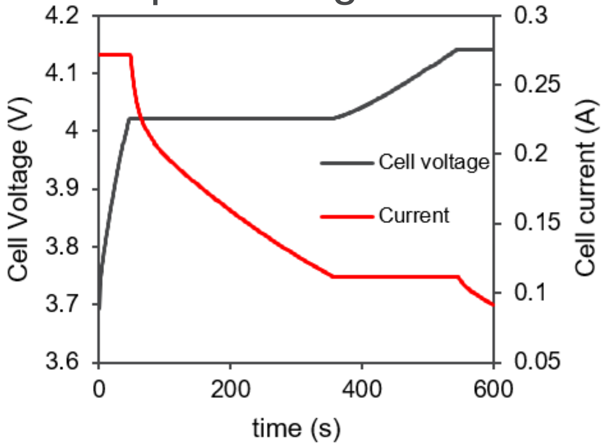
Example Ramp Protocol



7C + 0.25 mV/s ramping
Capacity = 1.80 mAh/cm^2
Min(φ_S- φ_E) = ~3 mV

Baseline 4.5 CCCV:
1.66 mAh/cm^2
Min(φ_S- φ_E) = 0 mV

Example 2 stage CCCV



CCCV1: 8.5C 4.022V
CCCV2:3.5C 4.14V
Capacity = 1.77 mAh/cm^2
Min(φ_S- φ_E) = ~1.8 mV

To prevent lithium plating, the cell should not be exposed to high current and high voltage at the same time

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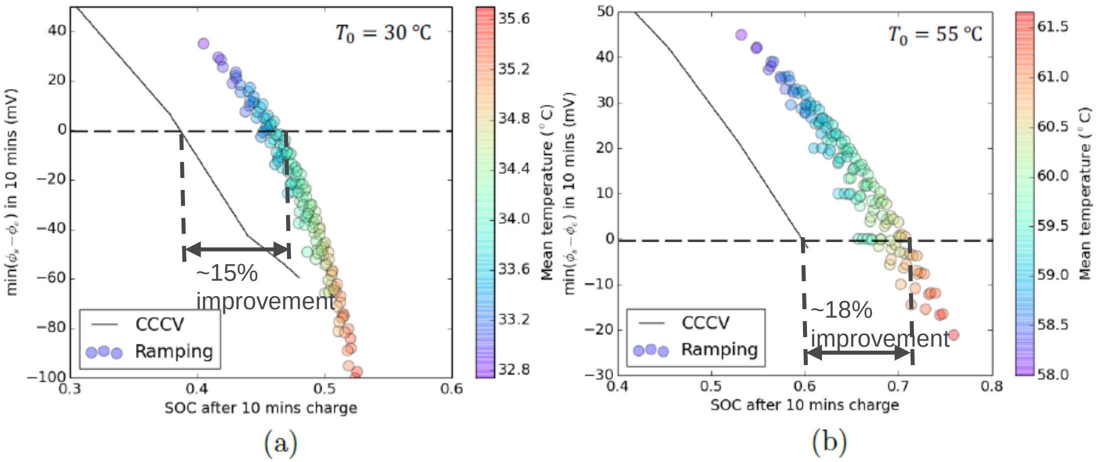
NOVEL PROTOCOLS ARE EFFECTIVE FOR HIGHER ENERGY DENSITY CELLS

Parameter sweep for ramp protocols for EV type cell at
a.) 30 °C
b.) 55 °C



- Higher loading cell: 4 mAh/cm^2 (110 micron electrodes; 230 Wh/kg with NMC 532)
- Improvement on no-plating capacity more significant for higher loading cell
- At 55°C, the no-plating capacity improved from 59% to 71%
- Improved charging protocol is roughly equivalent to raising initial charging temperature by ~10 °C
- Protocol eases requirements for elevated temperature or improvements to electrolyte/electrodes

For further details see: Mai, Colclasure, Smith, "Model-instructed design of novel charging protocols for the extreme fast charging of lithium-ion batteries without lithium plating," J. Electrochem. Soc.

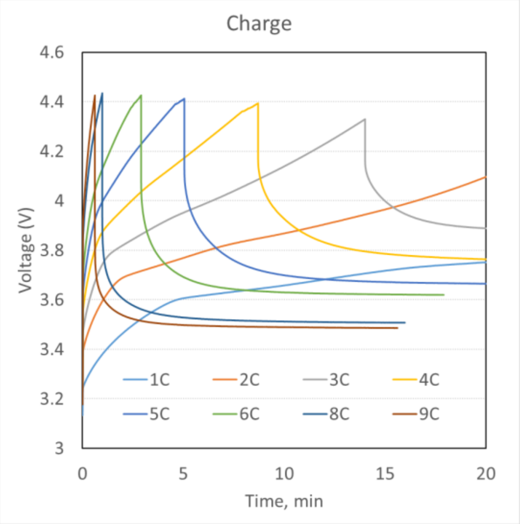
COIN CELL METHODS

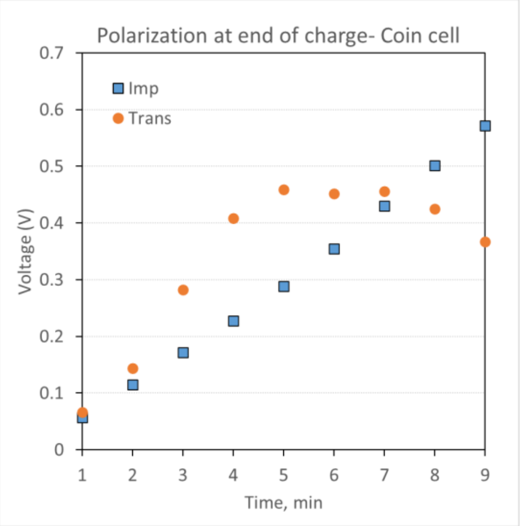
ALIGNING CELL DESIGN

Determining methods to better align coin and pouch cell data

- Charge coin cells to a scaled capacity based on pouch cell charge acceptance
  - Let Vmax float based on higher impedance
  - Use to refine charge protocols for evaluation in coin cells
  - Compare over voltage

Same trends, but elevated
Comparing with anode group on wetting and formation





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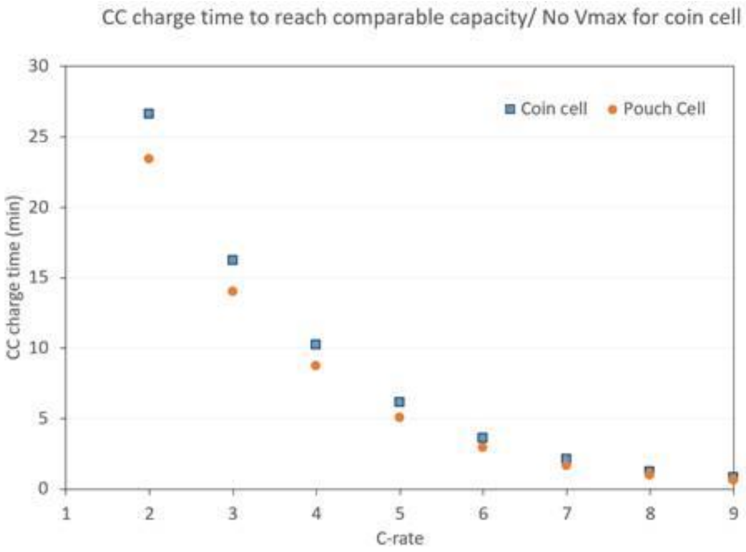
ALIGNING CELL DESIGN

Time spent in CC

- Close alignment in time during CC for both at high rates
- At lower rates longer time for coin cells
- Will be further refining based on formation/wetting discussion and additional post cycling comparison
- During Q3 will use modified protocols for extended analysis of charge protocols



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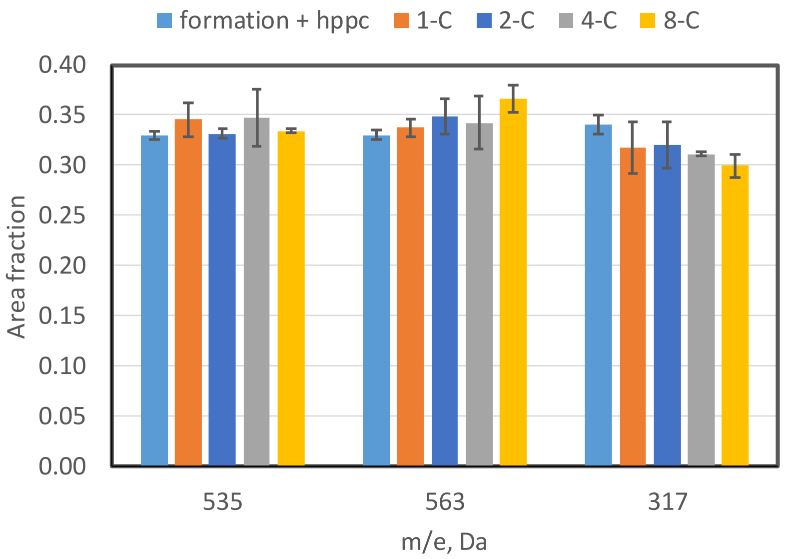
AFFECT CHANGES IN ELECTROLYTE COMPOSITION?

- Three organic compounds were found in the HPLC

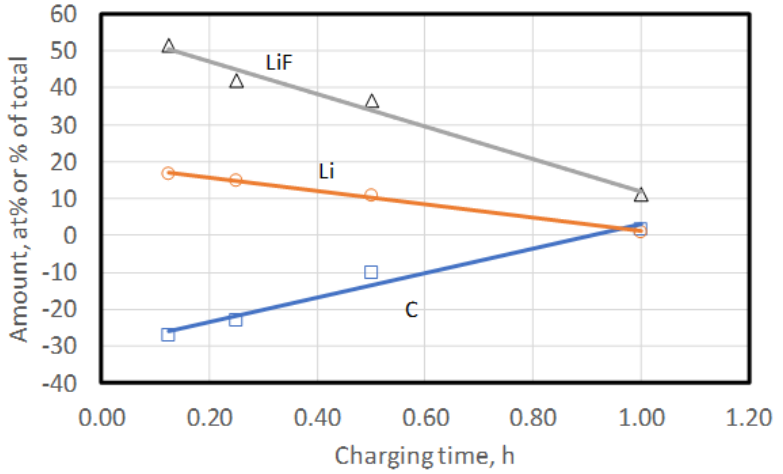


Observed weight, Da	Empirical formula	Calculated wt, Da
535	$C_{14}H_{34}O_{15}P_3^+$	535.33
563	$C_{16}H_{38}O_{15}P_3^+$	563.39
317	$C_{11}H_{23}O_7PF^+$	317.20

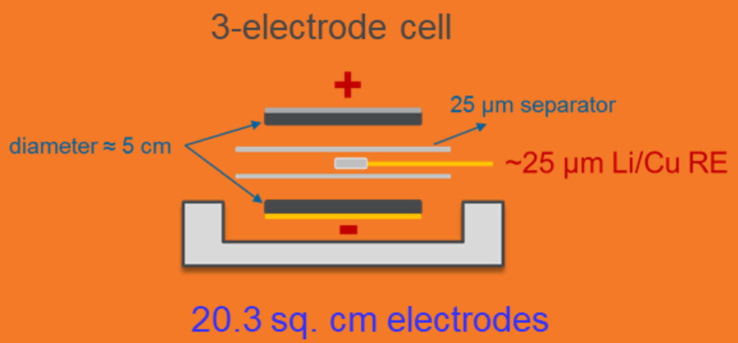
- No sensitivity to charge rate within experimental uncertainty

CHANGES ON ANODE SURFACE WERE SENSITIVE TO CHARGE TIME

- XPS results show that Li and LiF increase with decreasing charging time
- The total amount of carbon decreases with decreasing charge time
- Indicates that the surface layer is getting thicker and richer in LiF and other Li-containing species



THREE ELECTRODE ANALYSIS



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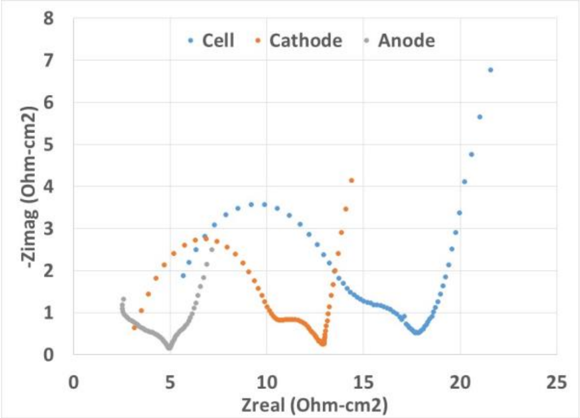
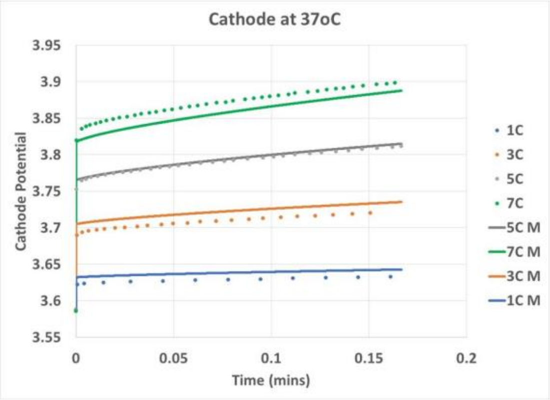
3 ELECTRODE SETUP TO OPTIMIZE MODEL PROTOCOL DEVELOPMENT

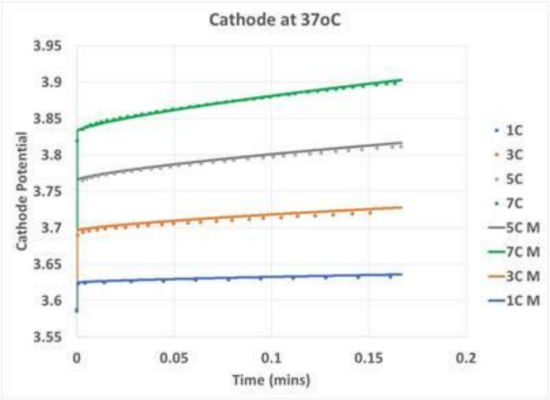
- Cell resistance is dominated by NMC cathode
- EIS and 10 s pulse data indicate cathode resistance is dominated by film resistance and not charge transfer reaction



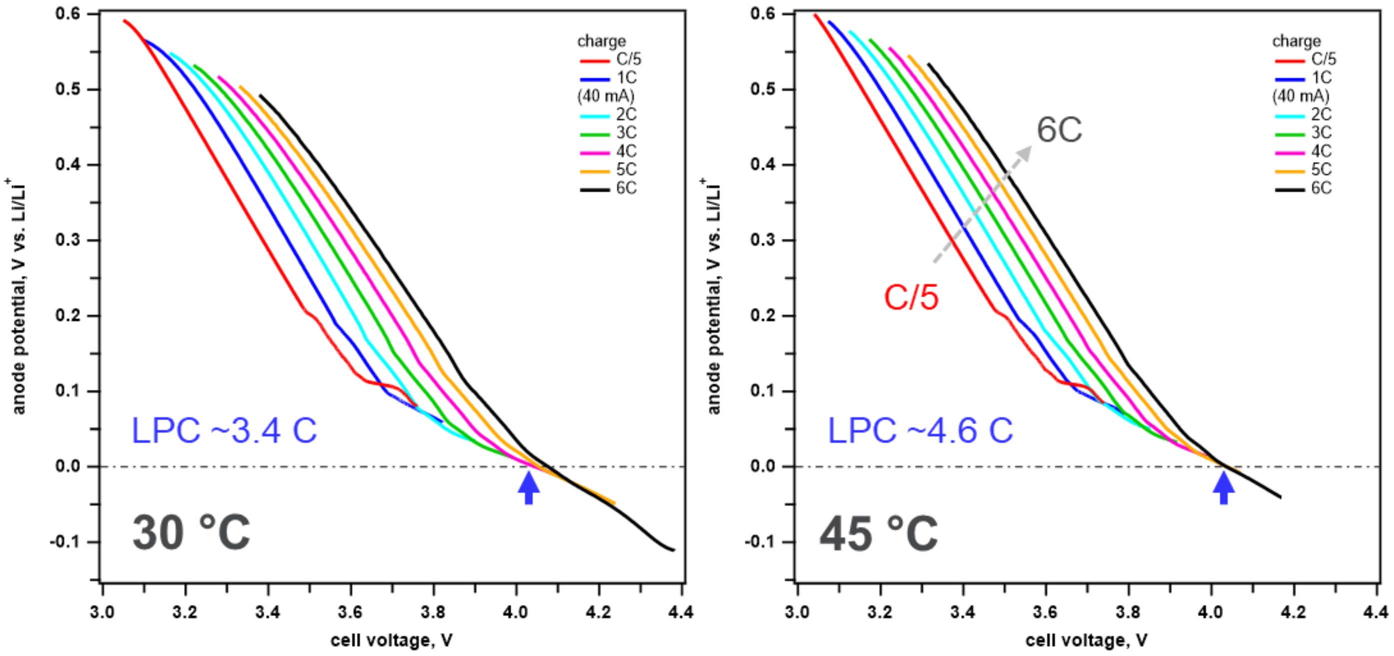
Model with no cathode-film resistance and only Butler Volmer Reaction



Model with cathode-film resistance and only Butler Volmer Reaction



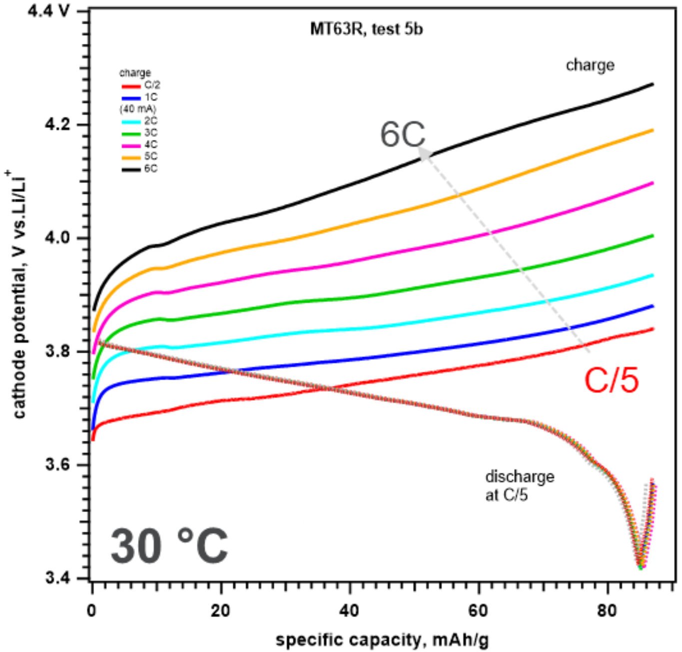
ANODE POTENTIALS VS. CELL VOLTAGE



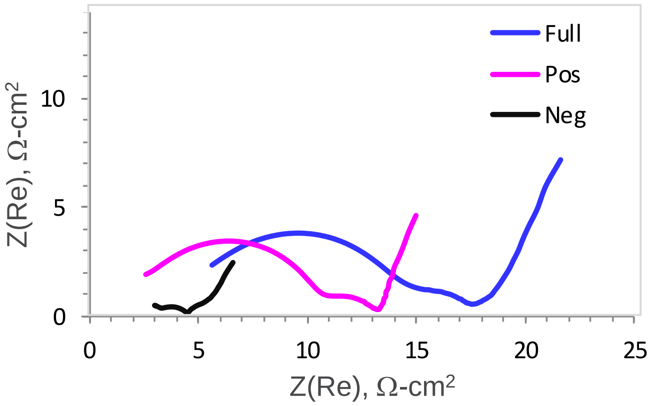
Limiting UCV to ≤ 4.0 V reduces likelihood of Li-plating (early cycles)

Lithium plating condition (LPC) - Arrow moves to lower voltages as cell ages

POSITIVE ELECTRODE – 30 °C DATA



Positive electrode polarization is responsible for most of the cell voltage polarization



Cell impedance is mainly from the positive electrode

High-frequency arc in EIS data suggests that the electrode impedance is mainly from the oxide/carbon interface

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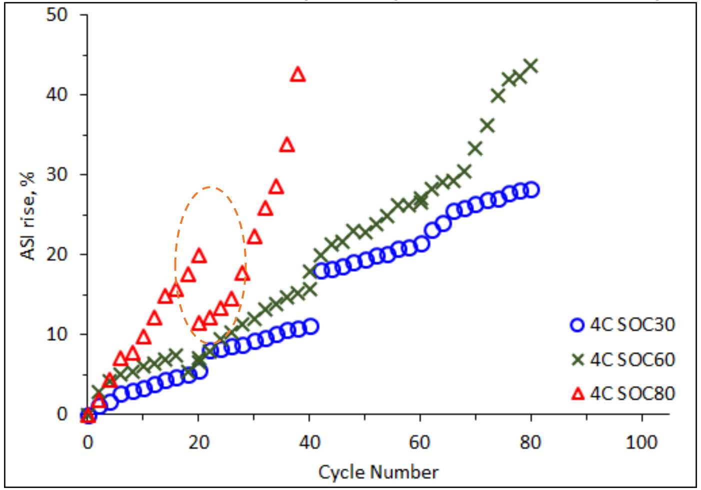
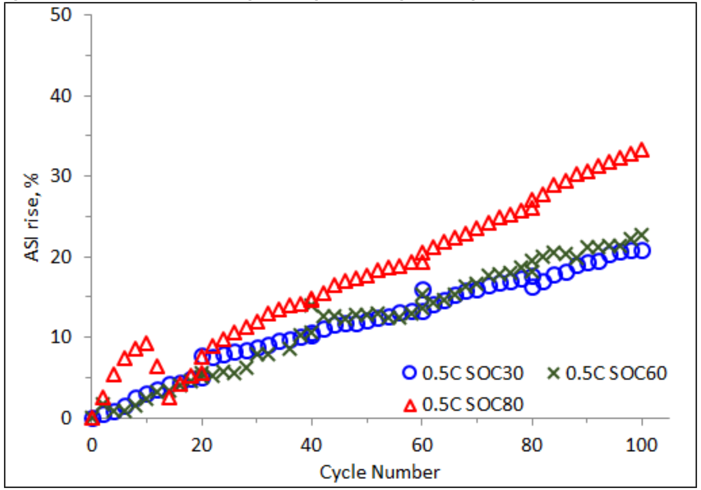
IMPEDANCE RISE TRENDS - EXAMPLE

3C 10s Discharge Pulse at 3.8 V

The impedance does not always show a steady rise; occasional drops and jumps are seen, especially after the C/25 capacity measurement (every 20 cycles).





In general

Wider the SOC range, faster the rise

Higher the rate, faster the rise

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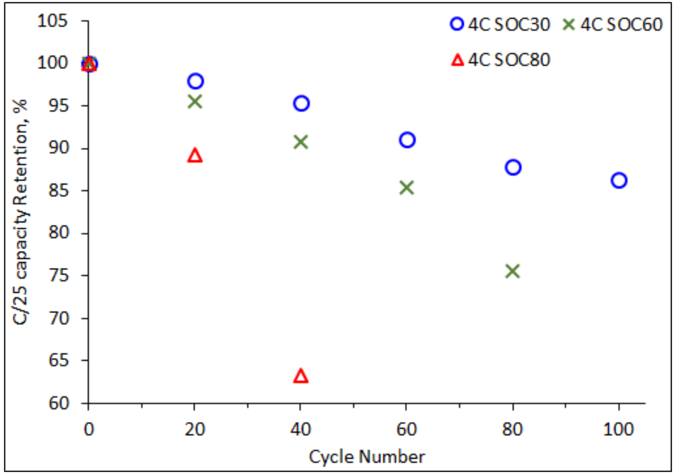
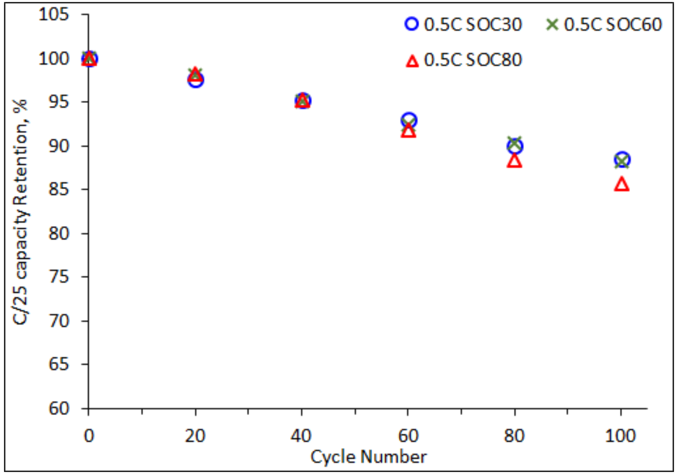
CAPACITY RETENTION TRENDS - EXAMPLE

C/25 discharge capacity





Effect of SOC range on cell capacity is more pronounced at higher rates. Li-plating is more likely when both SOC range and cycling rate are high.

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REMAINING CHALLENGES AND BARRIERS

- Transport is limited by cell design and materials – shifts in both can impact ultimate optimized protocol
  - Focus on tool development which can be broadly applied
- Refine understanding of electrolyte transport as anode task develops new formulations and compounds
- Continued refinement of full aging analysis including more direct experimental characterization for advanced protocols
- Understanding aging and implications of fast charge when not starting from 0% SOC

PROPOSED FUTURE RESEARCH

- Continue to expand fundamental understanding of charge protocols
  - Pulsed methods, temperature dependence etc.
  - Coordinate with anode and cathode tasks to understand variations produced by change in materials
- Expand evaluation for new charge protocols
  - Model developed systems
  - Updated temperature, cell composition (based on cathode and anode tasks)
- Expand characterization and aging analysis through joint electrochemical, post-test and modeling efforts
- Continued coordination with Grid & Infrastructure and Behind-the-Meter Storage Projects

Any proposed future work is subject to change based on funding levels

SUMMARY

- Established metrics for comparison of charge protocols
  - Aligned with both ability to fast charge and impact to aging
- Refined physicochemical models to generate information on electrohcmeical performance and heat generation
  - Validated with existing data
  - Used to identify new charge protocols for evaluation
  - Evaluation in process
- Refined methods using coin and three-electrode cells
- Transport still a key limitation that needs to be addressed and refined as new electrolytes and materials are introduced

CONTRIBUTORS AND ACKNOWLEDGEMENTS

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XCEL

eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

PUBLICATIONS AND PRESENTATIONS

Publications

- M-T.F. Rodrigues, K. Kalaga, S.E. Trask, D.W. Dees, I.A. Shkrob, D.P. Abraham, “Fast Charging of Li-Ion Cells: Part I. Using Li/Cu Reference Electrodes to Probe Individual Electrode Potentials” *J. Electrochem Soc.*, 166, A996-A1003 (2019).

- I.A. Shkrob, M-T.F. Rodrigues, D.W. Dees, D.P. Abraham, “Fast Charging of Li-Ion Cells: Part II. Nonlinear Contributions to Cell and Electrode Polarization” *J Electrochem Soc*, 166, A3305-A3313 (2019).

- I.A. Shkrob, M-T.F. Rodrigues, D.P. Abraham, “Fast Charging of Li-Ion Cells: Part III. Relaxation Dynamics and Trap-Controlled Lithium Ion Transport” *J Electrochem Soc*, 166, A4168-A4174 (2019).

- W. Mai, A.M. Colclasure, K. Smith, “Model-instructed design of novel charing protocols for the extreme fast charging of lithium-ion batteries without lithium plating,” J. Echem. Soc., accepted.

- A.C. Colclasure, T.R. Tanim, A.N. Jansen, S.E. Trask, A.R. Dunlop, B.J. Polzin, I. Bloom, D. Robertson, L. Flores, M. Evans, E.J. Dufek, K. Smith, “Electrode scale and electrolyte effects on extreme fast charging of lithium-ion cells,” *Electrochimica Acta*, 337 (2020) 135854.

- T. R. Tanim, P. Paul, V. Thampy, C. Cao, H.-G. Steinrück, J. N. Weker, M. F. Toney, E. J. Dufek, M. C. Evans, A. N. Jansen, B. J. Polzin, A. R. Dunlop, S. E. Trask, Heterogeneous Behavior of Lithium Plating During Extreme Fast Charging, *Cell Reports Physical Science* (under review, April 2020)

- T. R Tanim, E. J. Dufek, M. Evans, C. Dickerson, A. N. Jansen, B. J. Polzin, A. R. Dunlop, S. E. Trask, R. Jackman, I. Bloom, Z. Yang, E. Lee, Extreme fast charge challenges for lithium-ion battery: variability and positive electrode issues” *J Electrochem Soc*, 166 (10) (2019), A1926

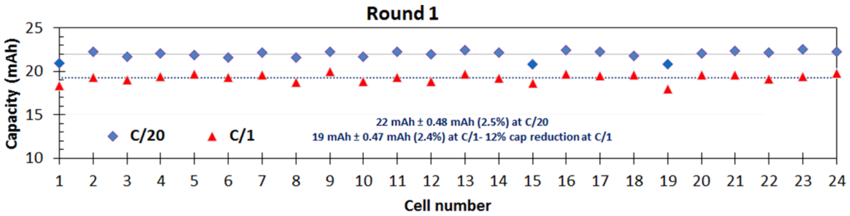
CRITICAL ASSUMPTIONS AND ISSUES

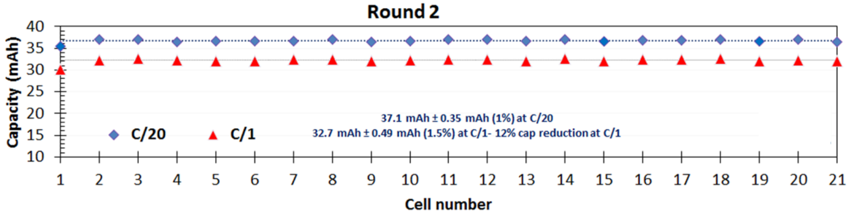
Major assumptions and issues listed earlier in the presentation

EXPERIMENTAL INFORMATION

Test set up and design

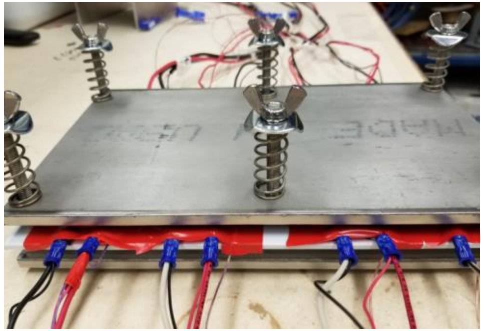
- Low variability as received
  - Round 1 – 1.9 mAh/cm^2
  - Round 2 – 3.0 mAh/cm^2



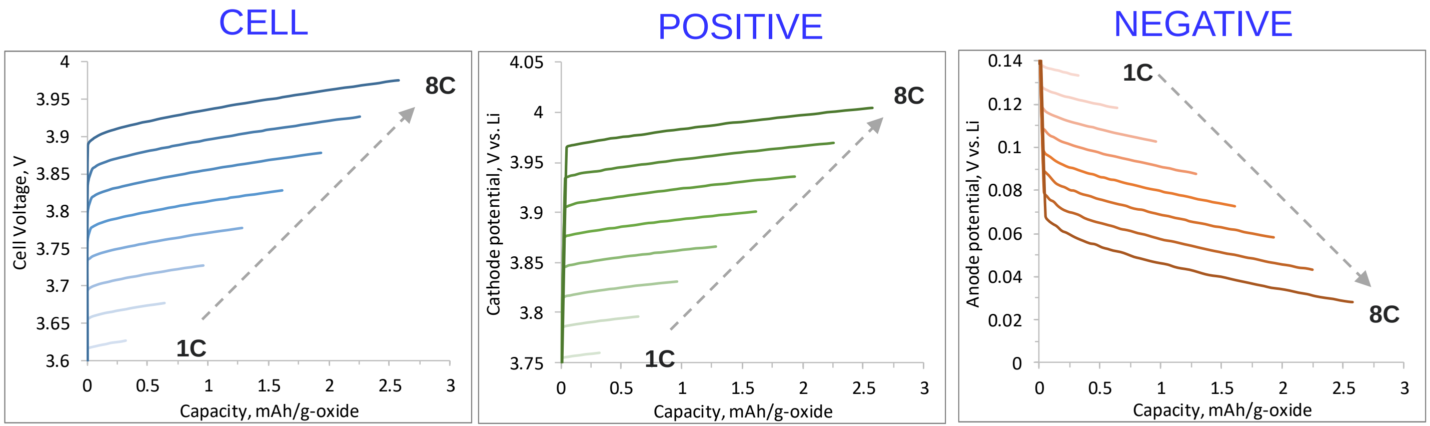


Lexan spacer

Polypropylene



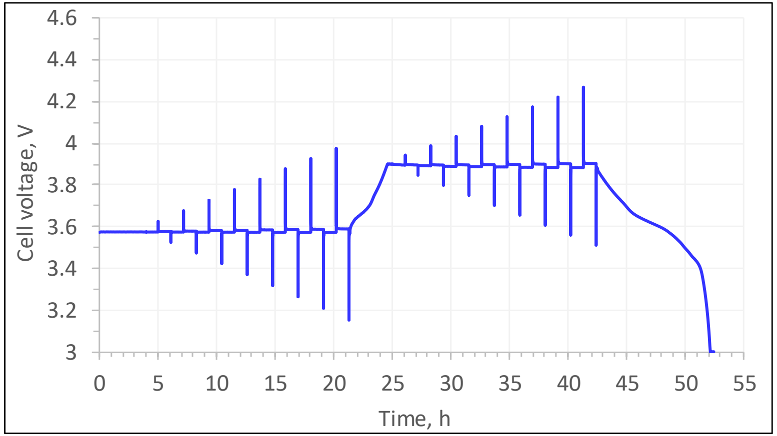
CURRENT PULSE EXPERIMENT – 3 ELECTRODE CELLS



10s charge and discharge pulses (1C – 8C) applied at ~3.6 V (cell voltage), 30 °C

Abraham - Argonne

TWO TYPES OF TESTS – ROUND 2 ELECTRODES

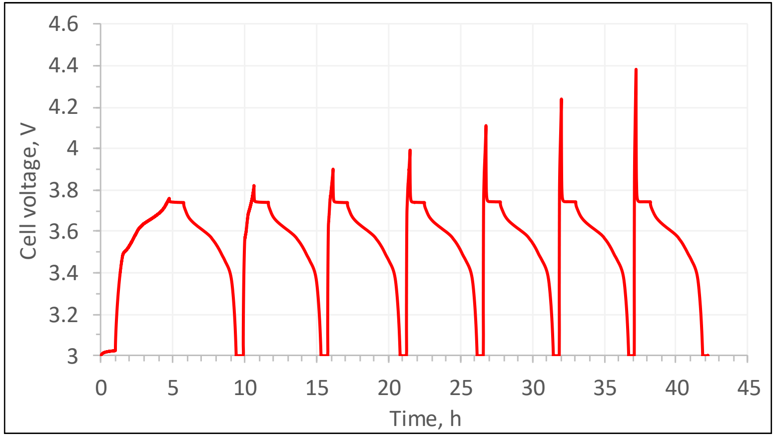


10s charge and discharge pulses (1C – 8C) applied at ~3.6 V and ~3.9 V.

Charge transfer during pulse 0.32 to 2.56 (~$Li_{0.01}$) mAh/g

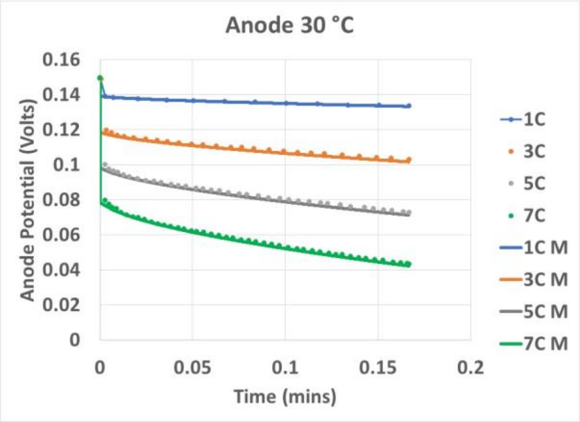
Capacity-limited charging to ~85 mAh/g (~$Li_{0.3}$) at rates from C/5 – 6C.

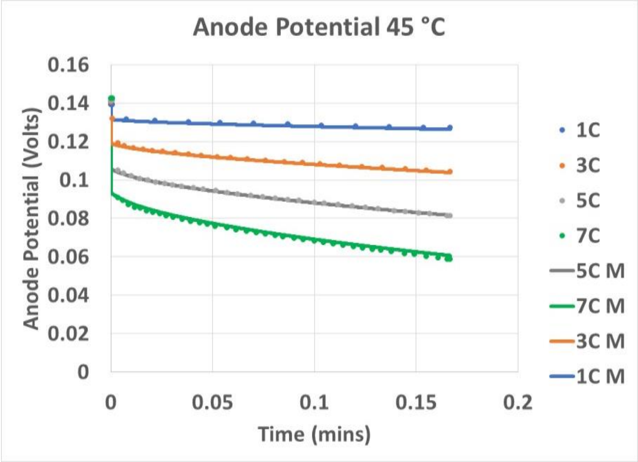
C/5 discharge to 3.0 V



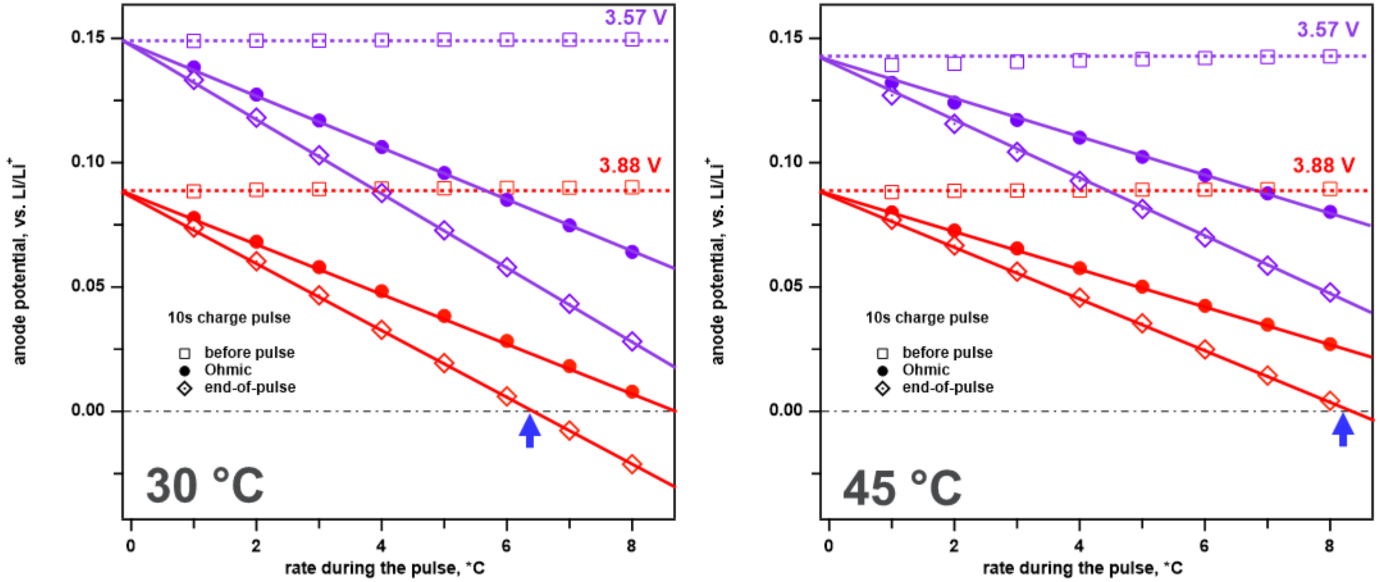
ACTIVATION ENERGIES FOUND FOR ANODE CHARGE TRANSFER

- Charge transfer chemistry found to be 30 kJ/mol
- Parameters consistent with10-minute 6C protocol measured at 20-50 °C
- Updated model will be used to evaluate charge protocols





PULSE TEST – 30 °C & 45 °C ANODE POTENTIAL



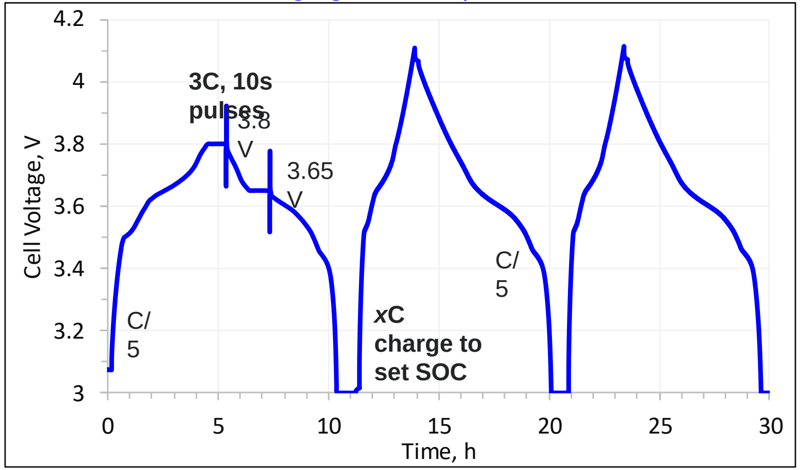
Li-plating condition (LPC) can be met during high-current pulses

- Depends on cell voltage; LPC met at ~3.9 V, but not at ~3.6 V
- Depends on length/duration of pulse (amount of charge moved)
- Depends on temperature; more likely at lower T's.

EXPERIMENT

Round 2 NMC 532 // Graphite full (coin) cells with Gen2 electrolyte
Formation: 2 C/10 cycles, 1 C/25 cycle

Aging Unit - Repeated



- 3C, 10s discharge & charge pulses every 2 cycles
- Cycles at varying charge rates to various SOCs
- Discharge to 3.0 V at C/5 until current < C/100
- C/25 every 20 cycles to check cell capacity
- Repeat steps until stop condition is reached

Cycling stopped when cell reached one of the following conditions
ASI >= 40 ohm-cm^2
Polarization during fast charge cycles >= 5V
Cycle count = 100

8C		30	20	10
6C		40	30	20
4C	80	60	40	30
2C	100	80	60	30
1C	100	80	60	30
C/2	100	80	60	30

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